



Experimental and theoretical investigation of nonconductive additives on the performance of positive lead acid battery plates

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HIGHLIGHTS

- Nonconductive additives of various sizes are tested in lead acid battery paste.
- Proposed model predicts utilization for batteries with nonconductive additives.
- Model predictions are comparable to measured battery discharge results.

ARTICLE INFO

Article history:

Received 28 September 2012

Received in revised form

17 November 2012

Accepted 3 December 2012

Available online 12 December 2012

Keywords:

Lead acid batteries

Additives

Nonconductive

Utilization

Life

Model

ABSTRACT

Additives can be added to lead acid battery electrodes to increase porosity and improve battery power and energy performance. This paper investigates the influence on electrode performance of different sizes and volume percentages of nonconductive additives to provide a clearer understanding of how they affect battery performance. The nonconductive additives used in the electrodes were hollow glass microspheres (HGMs). The solid volume percentages of various sizes of HGMs were varied from 5 to 60%. The discharge capacity for different volume percentages of the HGMs was measured in plates that were hand pasted to similar thicknesses. The utilization of active materials, which is defined as the ratio of the practical discharge ampere-hours over the stoichiometric capacity of the active materials, was plotted with respect to different solid volume percentages of additives. Experimental results were compared with the theoretical values of conductivity models. The change of utilizations with different solid volume percentages of additives compared favorably with the model predictions.

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1. Introduction

The lead acid battery has a number of properties that make it suitable to be used as an energy storage system: it has high cell voltage, high volumetric energy density, high power density, and the reactants are solids of low solubility. The reactions are also highly reversible which makes the batteries energy-efficient. Finally the production, storage, and disposal/recycling costs are low. However, the low specific energy (watt-hours per unit of battery mass) of lead acid batteries limits their application in more demanding situations such as electric and hybrid electric vehicles.

Berndt [1] estimated that the theoretical maximum specific energy of a lead acid battery is 166 Wh kg⁻¹ (75.4 Wh lb⁻¹). The actual specific energy available varies widely and is primarily

a function of the discharge rate. In practice, the available energy is usually less than 20% of the theoretical capacity. At lower discharge rates, the specific energy tends to be higher; as the discharge rate is increased, the specific energy decreases dramatically. Bode [2] estimated that the highest experimental utilization of the active material in the positive plate of a lead acid battery, lead dioxide (PbO₂), is about 55% even at very low discharge rates, and the maximum utilization of the active material in the negative plate (Pb) is slightly higher with a value of 60%.

The primary reason that lead acid batteries in their current state cannot achieve higher specific energies is that some of the active material in the electrodes does not react, and therefore the unreacted active material in both the positive and negative plates has not been discharged. Metzendorf et al. [3,4] attributed this phenomenon of incomplete reaction of active materials in the lead acid batteries to the change in the conductivity of active materials that occurs during the discharge process. As the active material

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Nomenclature

N	total quantity of nodes in the conductivity model
N_A	quantity of nodes replaced by additives in the conductivity model
f_N	fraction of nodes replaced by additives in the conductivity model
f_S	fraction of solid volume occupied by additives in the battery paste
f_T	fraction of total volume occupied by additives in the battery paste
U	utilization of the battery paste
$U_{\max}$	maximum utilization for paste without additives

discharges, it becomes an insulator rather than a conductor. When enough of the active material has reacted, portions of the remaining unreacted material become cut off from any available conductive pathway and are unable to react because current cannot transfer through this nonconductive, reacted active material. Although these non-reacting active materials still provide structural support and strength to the plates, their isolation by the reacted active materials prevents any further reaction from occurring; thus part of the theoretical capacity of the battery remains unused.

The maximum capacity available for reaction before conductivity limits the reaction is called the *critical volume fraction* which is defined as a ratio of the maximum capacity of the electrode divided by the stoichiometric theoretical capacity. The critical volume fraction is the highest utilization that can be achieved when the reaction is not limited by diffusion. This unreacted active material can be considered “dead weight” because it accounts on average for 40–50% of the total mass of the battery’s active material but contributes nothing to the specific energy of the battery during discharge. Different areas of active material may become isolated during each discharge cycle; however the overall maximum utilization remains consistent.

To reduce the dead weight, the effect of different additives on the performance and life of a lead acid battery has been studied by previous researchers [5–12]. Dietz et al. [5] summarized the effect of carbon black and silica gel on the performance and life of the positive paste. Baker et al. [6] concluded that synthetic graphite increased porosity and reduced structural coherence when it was used as an additive to tubular positive plates. Dr. Edwards et al. [7,8] found that the utilization of both positive and negative active material in lead acid batteries decreases at low specific rates with the addition of hollow glass microspheres (HGMs) to the paste. At high discharge rates, the utilization can be improved with the addition of HGMs. They attributed this improvement to the increase in the specific volume of the paste, which provides a better balance between the active material and the electrolyte in and near the plates. Kamenev et al. [9] showed the improved capacity and life characteristics of using high-collated carbon clusters as additives to electrode pastes. Valenciano et al. [10] increased the electrode capacity by using organic expander additives. Nakayama et al. [11] developed a battery for hybrid buses with carbon fibers in the negative plates. Hariprakash et al. [12] showed that it is possible to improve the positive active material utilization in lead acid batteries by coating Dynel fiber additive with tin dioxide.

Although a number of researchers have investigated various additives, both conductive and nonconductive, for use in lead acid battery paste, no general model has been developed and experimentally verified to predict the maximum plate capacity with the additives. This should not be a surprise as lead acid battery electrodes are complex systems and difficult to model. Researchers at

the University of Idaho have developed conductivity models that use a constant node size and other simplifying assumptions to predict the critical volume fraction of plates having additives [13]. Although these models provide an explanation for the maximum utilization of active material without additives and predict the utilization of electrodes with additives, these predictions are predicated on what the node size of the model should be. In a previous paper [14] a 3-dimensional conductivity model is developed and the node size was deduced from experimental porosity data for different node structures. Surprisingly, when a porosity of 50% is assumed, all of the physically realizable node structures result in critical volume fraction of approximately 60% with the estimated node size varying from 2 to 8 μm . The two-dimensional (2D) model described below also estimates a 60% critical volume fraction.

2. Model description

In previous research a two-dimensional (2D) conductivity model was developed to investigate the influence of spherical conductive and nonconductive paste additives [15], as well as paste additives with different aspect ratios (length to width ratio) [13] on the discharge performance of a lead acid battery. In this model, the following assumptions/definitions apply:

- The electrical conductive pathway is defined by a series of nodes; see Fig. 1.
- All nodes are the same size and are connected to the other nodes in a regular pattern.
- The nodes have no resistance when charged but are completely nonconductive when discharged.
- It is assumed that the reaction kinetics is not diffusion-limited; therefore, the active material reaction is limited only by the rate of electrical charge/discharge or the availability of a conductive pathway.
- *Utilization* is defined as the ratio of discharged nodes to the initial total number of available nodes; the critical volume fraction is the highest utilization that can be achieved and occurs when the reaction is limited by conductivity. Because the conductivity models only limit the reaction when conductive pathways no longer exist, the model always calculates the maximum utilization that is the critical volume fraction.

The conductivity model is based on the Monte Carlo method, which solves a problem by generating suitable random numbers and observing that fraction of the numbers obeying some property or properties. The model randomly chooses a node and attempts to

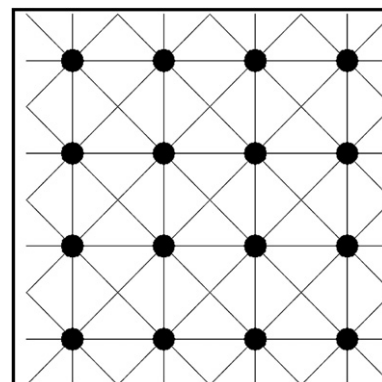


Fig. 1. Graphical depiction of the node structure used in the model.

find a conductive pathway to the edge of the grid. If a pathway could be found, the starting node is considered discharged and marked as nonconductive from that point forward. If a complete conductive pathway cannot be found, the starting node is then marked as isolated. After all nodes have been analyzed and all possible pathways have been tried, the model reports the total number of nodes that were discharged and isolated. In the remainder of this paper, the terms maximum utilization and critical volume fraction will be used interchangeably.

The conductivity model is used to characterize the influence of additives on the critical volume fraction. Nonconductive additives are modeled as non-reactive, always nonconductive nodes and are expected to reduce the critical volume fraction. Conductive additives are also non reactive, but would be always conductive and are expected to increase the critical volume fraction.

Fig. 2 shows the interaction of additives with the idealized paste structure that is assumed in the 2D model. This idealized model is very simple as all the active material nodes are assumed to be the same size and arranged in a constant structure (i.e. a simple cubic structure). In addition, although there is a distribution of particle size about the mean diameter for both active material and additives, all of the conductive and nonconductive particles added to the paste mixture are assumed to have the same mean diameter size. This simplified model does provide insight into the underlying structure of the electrodes and can provide quantified results [15–21].

Fig. 2 shows a small additive that is the same size as the nodes in the modeled paste (or a 1×1 node size additive). In the model, these small one node additives directly replace the active material and none of the porosity in the surrounding area. On the right is a large additive which displaces multiple nodes in the modeled paste. Not only does the large additive displace active material, it also displaces the microporosity surrounding the nodes to be replaced. Because of this, the number of nodes a large additive replaces will be less than the number of nodes that would have been occupied by the active material in the same volume.

Due to the nature of the conductivity model, the critical volume fraction is referenced to an additive node percent, or the percentage of nodes which were replaced by additives. This can also be represented as the fraction N_A/N , where N_A is the number of active nodes that the additive displaces, and N is the total number of nodes in the model. We will define this node ratio as f_N . For the purpose of this discussion, two other volume fractions must be defined. The first is the additive solid volume fraction, f_S , which describes the volume of additives in the mix compared only to the

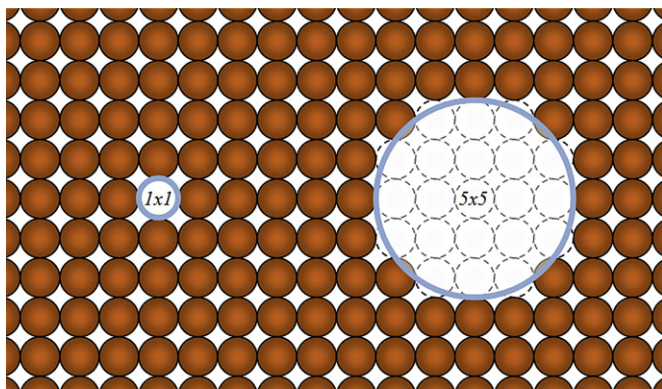


Fig. 2. Representation of two additives in the idealized paste structure. On the left is a small additive (1×1) which does not disturb the porosity of the paste while on the right is a larger additive (5×5) that displaces both the solids and the included microporosity.

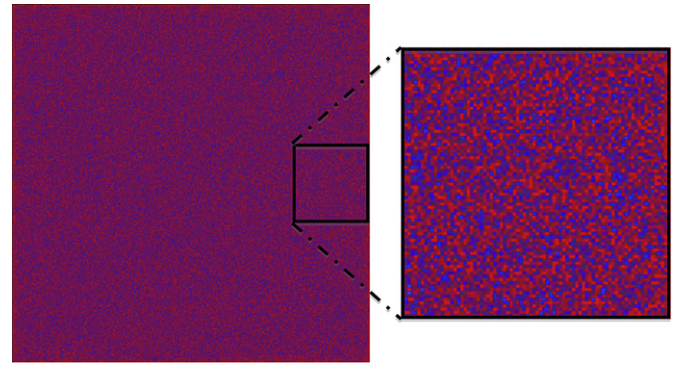


Fig. 3. Graphical output of the model for no additives with enlarged detail.

volume of the solids (i.e. it does not include the porosity). The second is the additive total volume fraction, f_T , which describes the volume of additives compared to the total volume of the paste, including porosity.

For small additives (i.e. 1×1 node additives) we expect the additive solid volume fraction, f_S , to be equal to the fraction of additive nodes, $f_N = N_A/N$. This is useful because the active material solid volume and the additive volume can be determined at the time of mixing. This implies that f_S is also known at the time of mixing and can be compared directly to the results of the model shown later.

For large additives that also displace porosity, the additive solid volume fraction, f_S , does not directly correlate to the fraction of additive nodes, f_N . For large additives, f_N would approach the additive total volume fraction, f_T , as the large additives are displacing both the active material nodes and the porosity in the paste. Unfortunately, f_T is not known at the time of mixing since the porosity is a function of many factors, and can vary from batch to batch. Because the porosity of the plates was not determined, only the solid volume fraction, f_S , was used in reporting our test results. As such, the number of nodes replaced by the larger additives would be over-estimated so the test results of the smaller additives should compare more favorably with the model than the larger ones.

Figs. 3 and 4 are graphical representations of the end result of a 2D model simulation after all of the available nodes have been discharged. Fig. 3 contains no additives and the utilization of active material is 60%. The standard paste model with no additives is used as the control simulation. This model result is very close to the 2D percolation theory prediction of 60% utilization. In Fig. 4 the yellow color represents the nonconductive additive which does not react, red is the reacted active material, and blue is the isolated active

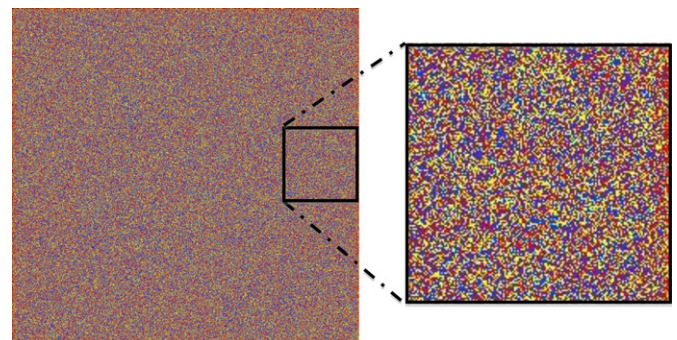


Fig. 4. Graphical output of the model for 1×1 aspect ratio (one node) nonconductive additives at 20% total paste volume with enlarged detail.

material that cannot react because there is no conductive pathway between it and the edge of the grid.

For a nonconductive additive that has a 1×1 node size, a 20% by solid volume loading (Fig. 4) reduces material utilization to 50% (a 10% reduction from standard paste) while still reducing the amount of lead weight by approximately 20%. Fig. 5 demonstrates the effect of additives on critical volume fraction for various sizes of nonconductive additives with an aspect ratio of one. For this aspect ratio, the figure shows the effect that different size particles have on both weight and utilization. However, all these results are scaled to the ideal diameter one node size-equivalent active material particle.

Zhang et al. [14] deduced from plate porosity data that the size of a single node in the crystal structure of the paste is approximately $1\text{--}10\text{ }\mu\text{m}$ in diameter. Therefore the 1×1 node size is representative of a particle diameter near $5\text{--}10\text{ }\mu\text{m}$; the 10×10 size is representative of a particle size nearer $50\text{--}100\text{ }\mu\text{m}$. The nonconductive paste additives chosen for the tests correspond roughly to the $10\text{ }\mu\text{m}$ size (i.e. the iM30K and Potters HGM additives) and $100\text{ }\mu\text{m}$ size (i.e. the K25 HGM additives). Although these additives have a distribution of sizes that are provided in Table 1, the iM30K and Potters HGM additives are approximated as 1 node and the larger K25 HGMs are approximated as 10×10 nodes each. These simplifying estimates were necessary in order to compare the experimental test results to the model.

For an identical volume percentage of two different sizes of nonconductive additives with an aspect ratio of one, the larger particles concentrate the nodes so that the additives are not as dispersed as when using the smaller particles. This causes the larger nonconductive particles to have less effect on the critical volume fraction or active material utilization than the smaller particles. The strategy suggested by the simplified model, therefore, is to use large nonconductive HGMs or porous, hollow glass microspheres (PHGMs) for structure and filler so that the effect on the critical volume fraction is minimized.

The effect that the one node size (1×1) equivalent nonconductive additives have on the critical volume fraction (CVF) or the maximum utilization, $U(f_N)$ of the active material can be described by the following equation.

Table 1
Specifications for nonconductive additives.

Group	Density (g cm^{-3})	Top size (μm)	Average size (μm)	Effective node size
3M K25	0.25	105	50–70	10×10 nodes
3M iM30K	0.63	26.7	12–18	$\sim 2 \times 2$ nodes
Filtered 3M iM30K ($20\text{ }\mu\text{m}$)	0.285 (est.)	20	10–12 (est)	1×1 node
Potters	2.5	10 (est.)	5–7	1×1 node

$$U(f_N) = \frac{(U_{\max} - f_N)}{(100\% - f_N)} * 100\% \quad (1)$$

$U_{\max}$ is the maximum utilization or CVF achievable when making standard paste having no additives. For the model, $U_{\max}$ is approximately 60% and f_N is the node ratio discussed earlier. The equation's numerator represents the amount of active material that can react while the denominator is the total amount of active material. Because the additive size is the same as the node size, an equal volume of active material will be displaced by the nonconductive additives reducing the active material that can be discharged. Eq. (1) only applies to single node equivalent size additives and no comparable equation has been found for larger node size additives.

A comparison of the predictions of Eq. (1) and the numerical model predictions [15–21] are shown for the $U_{\max}$ value of 60% in Fig. 5. As the figure shows, Eq. (1) fits the model predictions very well except at the high loadings of additives. This discrepancy can be attributed to the “edge effect” since the material near the edges is always in contact with the conductive grid surface. Therefore, even at high loadings, the edges of the plate will always be available for discharge even when large areas of the active material further from the outer edge will be cut off due to the nonconductive additives.

When the experimental values of the maximum utilization, $U_{\max}$, in Eq. (1) is different from the 60% model estimate, we use the experimentally measured maximum utilization in Eq. (1) to estimate the relationship between utilization and volume percent of

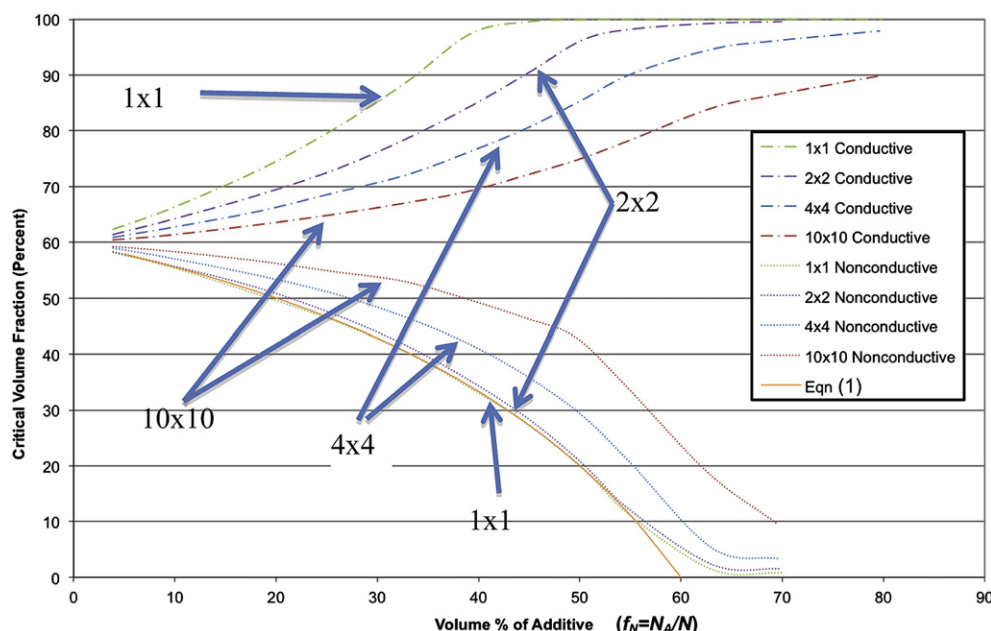


Fig. 5. Critical volume fractions for different size additives with 1×1 aspect ratio.

additives for one node additives. In this manner, the result for Eq. (1) when no additives are used (i.e. $f_N = 0$) is simply the observed utilization. This scales Eq. (1) to the experimental maximum utilization so that the curve crosses the x -axis at the experimentally determined utilization.

Using Eq. (1) with the experimentally determined maximum utilization allows us to compare hand pasted plates that contain additives to plates having no additives whose utilization is less than 60%. Two different standard pastes having no additives were formulated and tested. The first paste formulated had a maximum utilization of 47%. The paste with no additives having a critical volume fraction of 47% was associated with the early batches of paste which had the small additives. The standard paste having no additives that was formulated later achieved 55% maximum utilization, and this 55% critical volume fraction was associated with the later batches of paste which had the large additives. Assuming that all plates fabricated at approximately the same time should have standard paste that behaves in the same manner, then the discrepancy in the two utilizations is attributable to the skill and practice of graduate students performing the hand pastings. The students improved with practice and were more skilled when the standard and large additives were formulated and pasted. Therefore, the maximum utilization of 47% was used as the reference for the smaller additives while the maximum utilization of 55% was used for the larger particles.

Fig. 6 illustrates a comparison of the effect of additives on the critical volume fraction as a function of different aspect ratios of nonconductive additives. This image was created using test runs of the model for the indicated aspect ratio of conductive and nonconductive particles at volume percent varying from 5% to 70%. The model predicts that large aspect ratio nonconductive additives quickly “fence off” large areas of the available active material in the 2D model; this effect leads to low utilization. Smaller aspect ratios of nonconductive fibers do not reduce utilization as much as the higher volume percent of the nonconductive additives. This result shows that when the aspect ratios are small (i.e. $<1 \times 3$) the results are not much different than additives having an aspect ratio of one. Although some of the small additives were slightly elongated, assuming an aspect ratio of one appears to be warranted.

When long conductive fibers are used, they help prevent large areas of the plate from being isolated. As shown in Fig. 6 the utilization quickly climbs to 80% with only 13% by volume of 1×100 conductive fibers and falls to 8% utilization with the same amount of nonconductive fibers. The modeled results for aspect ratio and size effects of conductive additives found in Figs. 5 and 6, as well as the effects of nonconductive additives with different aspect ratios found in Fig. 6 are included for completeness but are not experimentally investigated in this paper.

3. Experimental setup

In our tests, the 3M K25 and filtered iM30K HGMs and Potters Spherglass HGMs were used as the nonconductive additives in the paste. The manufacturer's specifications for these HGMs are shown in Table 1 along with information about the filtered iM30K HGMs. The average particle size of the 3M model K25 HGM is between 50 and 70 μm with a bulk density of 0.285 g cm^{-3} . The filtered iM30K HGMs had an average particle size of near 5–10 μm with a bulk density of 0.32 g cm^{-3} . Both the K25 and iM30K HGMs were provided by 3M Corporation. Potters Brand HGMs have an average particle size of about 3–5 μm with some larger clustered particles.

The performance of electrodes having different amounts of HGMs in the paste was evaluated by cycling the electrodes at low discharge rates (i.e. $C/10$ – $C/20$ rates). The iM30K glass bubbles were filtered through a 20 μm filter supplied by BioDesign, Inc. to obtain a useful bulk of glass microspheres with a diameter less than 20 μm . As shown in Fig. 7, the maximum size of the filtered iM30K is approximately 20 μm . Based on the specifications of the bulk iM30K composition as provided by 3M, the average glass microsphere diameter of the 20 μm filtered iM30K spheres is approximately 12 μm . Fig. 8 is an SEM of the as-received Potters HGMs and Fig. 9 is an SEM of the as-received K25 HGMs.

The HGMs have a solid surface so no electrolyte can penetrate them. Since the HGMs are chemically inert in the battery environment and nonconductive, the only parameters varied by the addition of the HGMs is paste density. Therefore, the effect on the utilization capacity of different volume percentages of the HGM sizes can be studied independently as all other variables are kept constant.

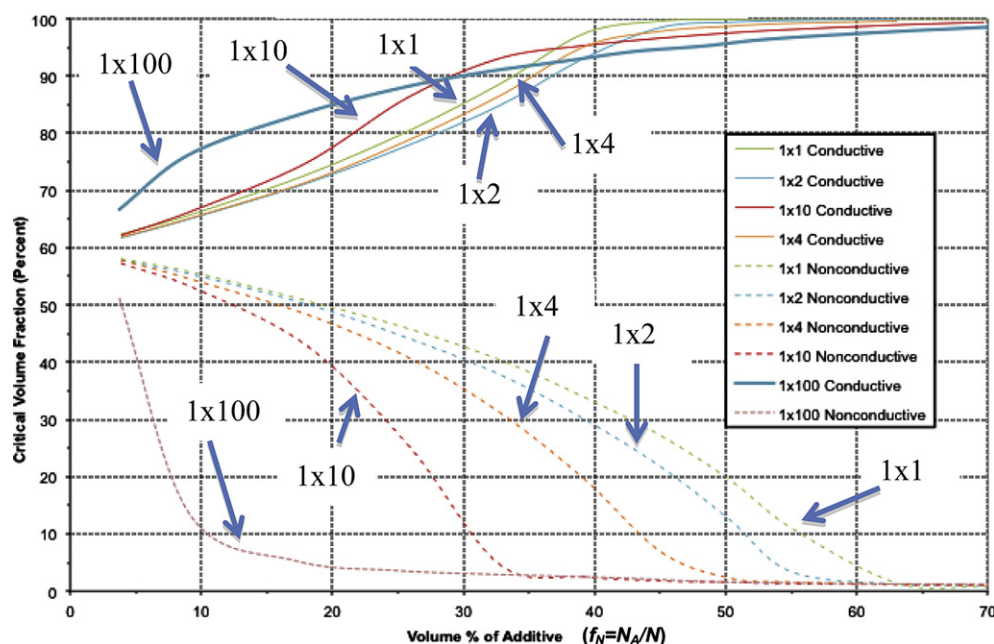


Fig. 6. Critical volume fractions for different additive aspect ratios.

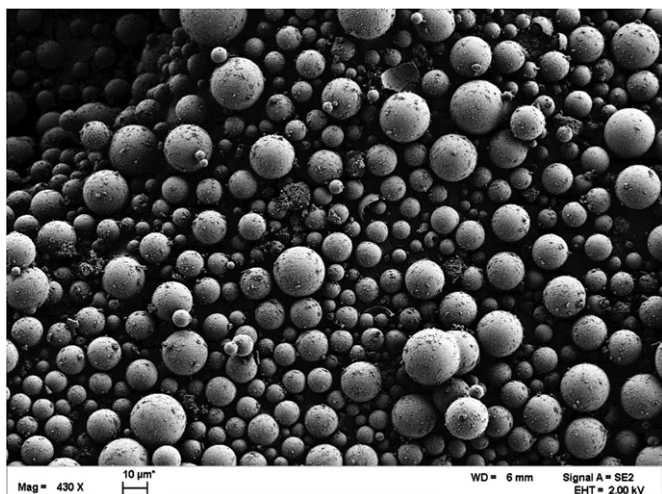


Fig. 7. <20 μm filtered 3M iM30K HGMs.

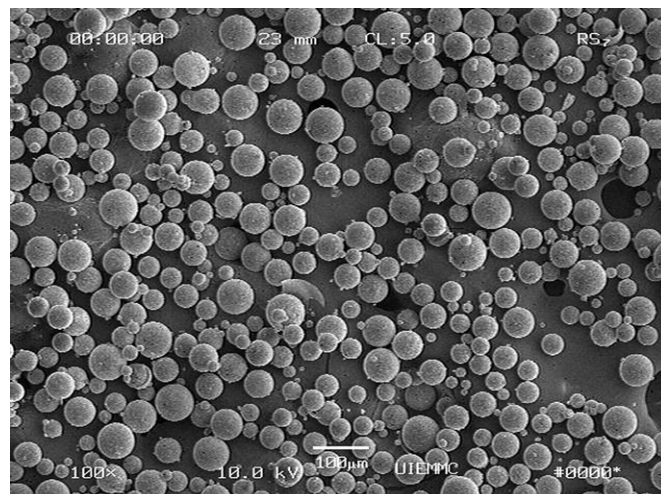


Fig. 9. 3M K25 HGMs.

The paste density of plates without glass microsphere additives was 4.27 g cm^{-3} (70 g in^{-3}) and was similar to that used in production plates. The additive solid volume fraction, f_s , of the several sizes of HGMs added to the battery paste varied from 5% to 60%. All of the electrodes (or “plates”) used the same production grids and had identical dimensions. Positive plates with and without HGMs were hand pasted so that they could be compared directly. The hand pasted positive plates without HGMs were also compared with equivalent, machine pasted, production plates provided by a battery company to ensure that the manual pasting could be reasonably compared to standard production plates.

Two sets of hand pasted plates without additives were tested. The first set was fabricated at the same time that the paste containing the smaller, 1×1 node additives (i.e. the iM30K and Potters Spherglass) was made. These hand pasted plates without additives act as the baseline for the plates having the 1×1 node sized additives. Later, when the paste having larger K25 additives was made, another batch of paste having no additives was fabricated and tested. This second batch of paste without additives acts as the reference for the plates having the K25 additive.

The critical volume fraction for the hand pasted plates associated with the small additives was 47%, while the critical volume fraction for the hand pasted non-additive plates associated with the larger

additives was 55%. The 55% critical volume fraction is consistent with Bode’s estimate of the maximum utilization of positive plates and is also consistent with standard factory production plates (56% utilization). Since the model has many simplifying assumptions, including zero resistance for charged plates, the baseline estimate of 60% for the critical volume fraction is higher than observed for positive plates. Because of this discrepancy, a baseline paste having no additives was used for comparing the model’s estimates to the experimental results. The critical volume fraction for the hand pasted plates having no additives is essential when comparing experimental results for different size additives and volume percent loadings with the model.

4. Paste mixing procedure

A Barton-type lead oxide was used to formulate the paste. The HGMs were mixed with the dry lead oxide powder before the water or acid was added. For every pound of lead oxide in the paste mix, 30 ml of sulfuric acid (density 1.4 g cm^{-3}) was added over a 3-min period, and then 60 ml deionized water was added over a 5-min period. In the initial reaction of sulfuric acid with lead oxide, both small-crystallized tribasic sulfate and bulk-crystallized tetrabasic sulfate were formed. To drive the reaction to form the tribasic sulfate, the temperature of paste was kept below 70°C during mixing. Additional water was added to the mixed paste until the desired paste density was obtained. In our experiments, the baseline ratio of the volume of additional water to the volume of additives was approximately 1:1 with minimal amounts of additional water added as needed to ensure a pasteable texture. A standard home mixer was used to mix the paste, and the paste density was determined by weighing a given volume of the wet paste. For paste with HGMs, the optimal paste density occurred when the paste density stopped increasing with the addition of water and started to decrease. This density occurs when the lead oxide particles begin to “float” out of the paste or when the additional water is increasing the volume and not filling in between the other paste particles. The density of the baseline paste having no additives is about 4.27 g cm^{-3} (70 g in^{-3}).

5. Cell fabrication procedure

Plates were fabricated with the above-described hand pasting procedure using standard production grids. The cast grids used in production plates had dimensions of 8.55 cm (3.37 in.) high,

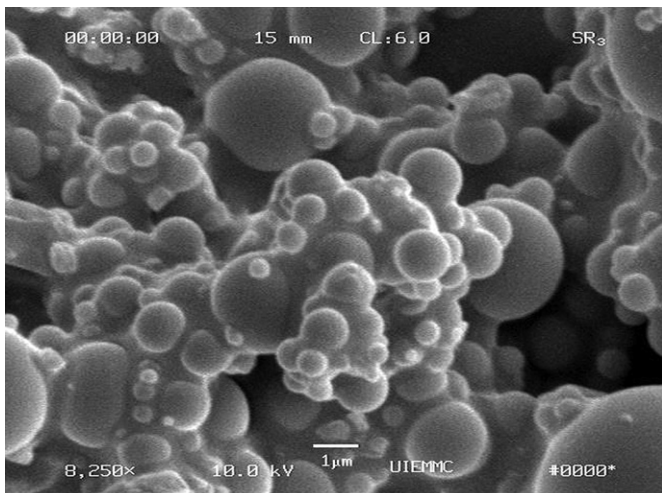


Fig. 8. Potters’ nonconductive glass additives.

9.27 cm (3.65 in.) wide, and 0.114 cm (0.045 in.) thick, and weigh 21 ± 0.5 g. The grids were composed of a tin lead alloy. The thickness of the pasted production positive plates was about 0.13 cm (0.05 in.), and the hand pasted positive for comparison were over pasted on both sides of the grids and the final thickness of the hand pasted plates was close to the production plate thickness of 0.13 cm. After pasting, the plates were wrapped in paper and put into a pressure cooker for hydrosetting and cured for about 24 h. The plates were then left in a temperature control oven that was set at 37.8°C (100°F) for another 24 h. After this curing process, each plate lost 2.5–2.8 g of weight. The purpose of the curing process was to produce hand pasted plates that performed similar to the production plates.

A minimum of three cells were fabricated for each plate type, each containing one positive hand pasted plate and two factory-pasted and preformed production negative plates. Positive and negative plates were separated by one layer of glass mat separator and two layers of polyethylene separator which provided a separator thickness of 0.17 cm (0.067 in.). The electrodes were large enough to more than fully discharge the positive plate in each cell. The total acid stored in the separators and other empty cell volume was approximately 230 ml. Each cell was therefore designed to contain excess electrolyte and negative active material to ensure that the positive electrode was the limiting electrode.

6. Charging and cycling procedure

The one-shot method was used in the formation charge process. The cell was filled with H_2SO_4 at a concentration of $\sim 1.28\text{ g cm}^{-3}$. The charging ampere-hour calculations are based on the amount of active material that each cell has in its positive electrode. Each cell was charged at a constant current based on 35% stoichiometric capacity for up to 1 h with a cutoff voltage limit of 2.35 V. Then the cell was switched to a second constant current charge step based on 40% of the stoichiometric capacity returned over 4 h with a cutoff voltage limit of 2.5 V until 105% of stoichiometric capacity was exceeded. All formation charges were performed at an ambient temperature of 37.8°C (100°F).

After the formation charge, the cells were cycled with automated cycling equipment. The cycle tests consisted of constant current discharge at the 20-h discharge rate. All discharges were terminated at the lower limit cutoff voltage of 1.75 V. After each discharge, the cell was charged at constant current where the current was chosen to return 40% of the stoichiometric capacity over 4 h until a cutoff voltage limit of 2.45 V was reached. The cell voltage was held constant at 2.45 V until 115% of the previous discharge cycle ampere-hours were returned and the cell current was below 0.4 A.

For the first 2 or 3 cycles, the final constant voltage charge step was ended when the current reached the 0.4 A lower current limit, and during the following cycles, the final constant voltage charge step was ended by the 115% overcharge limit. Each charge and discharge step was separated by a rest step of 1 h for electrolyte equalizing. All charge and discharge tests were performed at an ambient temperature of 37.8°C (100°F). The cell voltage, current, charge and discharge ampere-hours, and internal resistance were recorded at each charge and discharge step.

7. Results and discussion

Figs. 10–12 are SEM pictures of plates after 30 cycles with 27%, 39%, and 59% volume of K25 HGM additives, respectively. These pictures were taken to show that the HGMs survived the pasting and cycling processes. If all the HGMs had broken, then the volume of active material in the plates would not have been affected much,

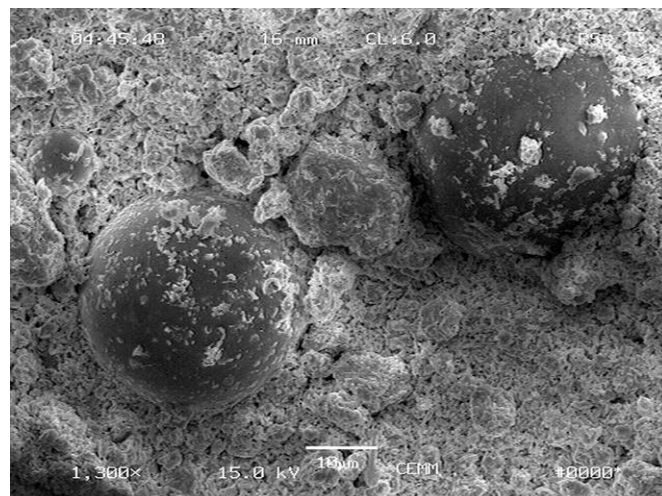


Fig. 10. SEM of 27% K25 HGM paste.

and the addition of the HGMs theoretically would have had very little effect on paste performance.

In the test cells, a single unformed hand pasted positive plate and two preformed production negative plates were discharged at the approximate 20 h rate to determine their maximum utilization. Control cells made of unformed production positive plates having no additives had utilizations of 56%. This number is very close to the number Bode expected, and, based on Metzendorf's theory, the discharge capacity is the critical volume fraction of the plate. Cells consisting of one hand pasted positive plate with no additives and two preformed production negative plates were also fabricated and tested. Hand pasted positive plates with nonconductive additives in the paste were then fabricated with varying amounts of additives ranging from 0 to 60% by solid volume and tested.

As mentioned in the [Model description](#) section of this paper, the data presented in [Figs. 13 and 14](#) are compared to the additive solid volume fraction, f_s , for all additives regardless of size. For the filtered iM30K HGMs and the Potters Spheriglass HGMs, it was expected that f_s was equivalent to the additive node percent as discussed earlier. For the 3M K25 HGMs which are considerably larger, it is expected that the additive node percent be less than f_s and greater than f_T . As a result, the performance of the larger spheres is likely to be overrepresented on the figures.

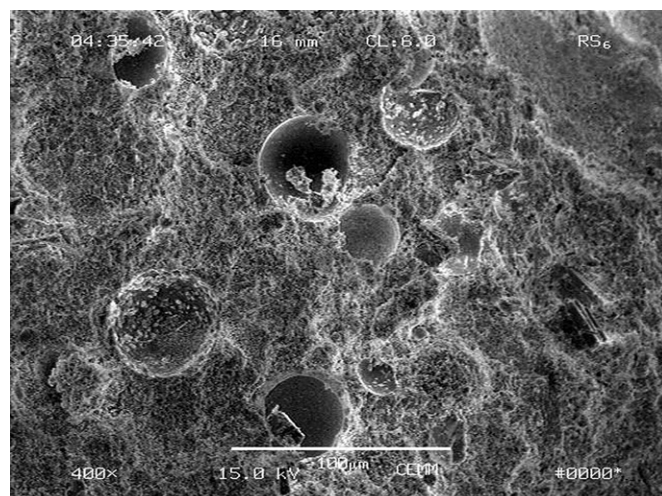


Fig. 11. SEM of 39% K25 HGM paste.

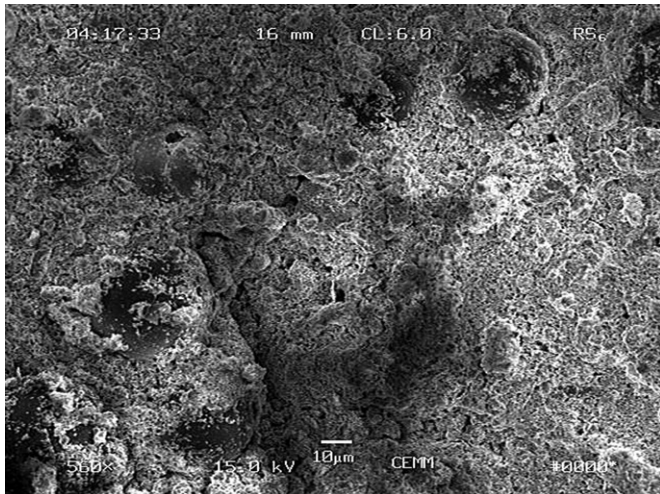


Fig. 12. SEM of 59% K25 HGM paste.

Fig. 13 shows the experimental results of cycling the different paste mixtures compared to the model predictions and the predictions of Eq. (1). This figure plots the positive electrode active material utilization against the solid volume percentage of HGMs added to the paste. Utilization is determined by dividing the discharge capacity by the stoichiometric capacity of the paste. The maximum critical volume fractions for the paste without additives made during the production of the K25 HGM paste batches and the iM30K HGM paste batches are represented by the symbols on the Y-axis (Baseline – K25 and Baseline – iM30K & Potters, respectively). The standard deviations for the plates are also shown in the figure. The standard deviation for each type of plate tested was less than $\pm 5\%$ and typically less than 3%. The

standard deviation for each point is the combined average standard deviation in utilization when cycling for all cycles and all plates of a given paste type.

We believe the differences between the experimental and model results are primarily due to the model's simplifying assumptions and the difference between the batches of paste regardless of the addition of any additive. When hand pasting non-additive (standard) active material, the utilization of the plate can vary due to differences in age of lead oxide, porosity, curing variables (temperature, time), electrolyte concentration and the ability of the lab personnel pasting the grid with the active material.

A batch of paste fabricated without additives at the same time as the iM30K and Potters HGM batches had maximum utilizations on average of 47%. Since the maximum utilization for the active material without additives made at the same time we were pasting the iM30K and Potters HGMs was 47%, we would expect the curve representing 47% maximum utilization (Eq. (1) with $U_{\max} = 47\%$) to be a reasonable approximation to the data for these plates. In Fig. 13, $U_{\max}$ values of 45%, 55%, and 60% are used in Eq. (1) and plotted with the experimental 1×1 node data. For each curve, the maximum utilization is achieved at zero percent HGMs and the utilization falls to zero where the volume percent of HGMs in the paste matches the $U_{\max}$ value. As can be seen from Fig. 13, most of the data points for the iM30K and Potters pastes lie between the 47% and 55% utilization curves predicted by Eq. (1). These results show that Eq. (1) approximately predicts the behavior of 1×1 node size nonconductive additives when the $U_{\max}$ value for the hand pasted plates is known.

A batch of paste without additives made at the same time as the K25 HGM batches had maximum utilizations on average of 54%. The utilization is consistent with Bode's experimental results that the maximum utilization for positive plates was 55% and also compares favorably with the production positive plates (56%). For these reasons, we compare the paste batches containing the K25

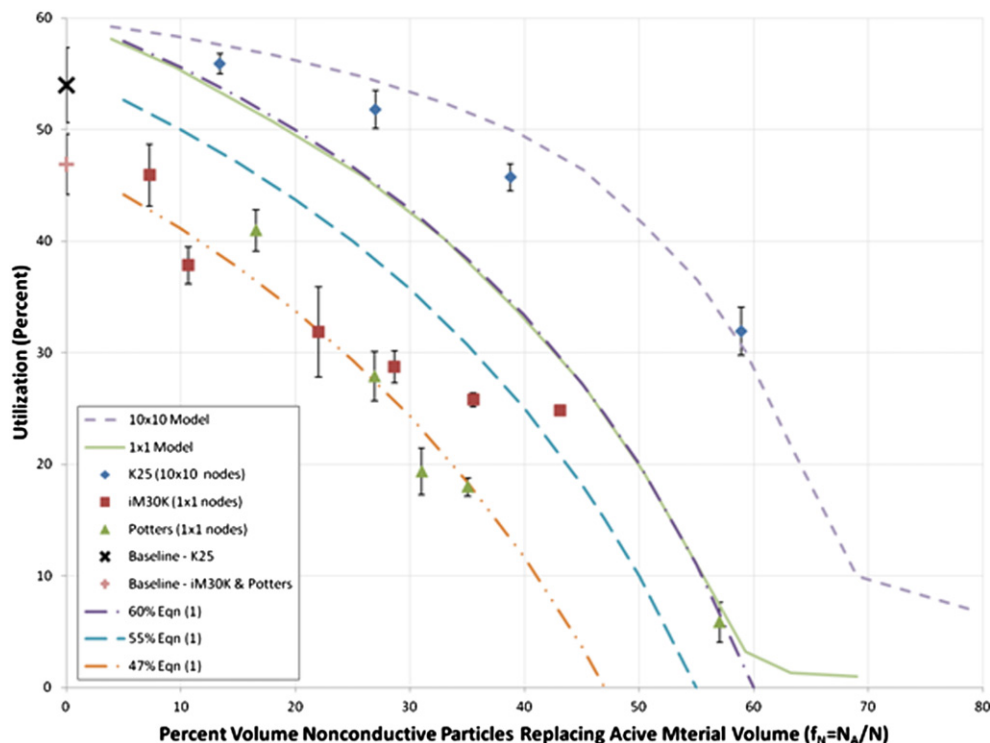


Fig. 13. Model predictions and Eq. (1) predictions vs. experimental results for utilization of paste containing nonconductive additives at various volume percentages.

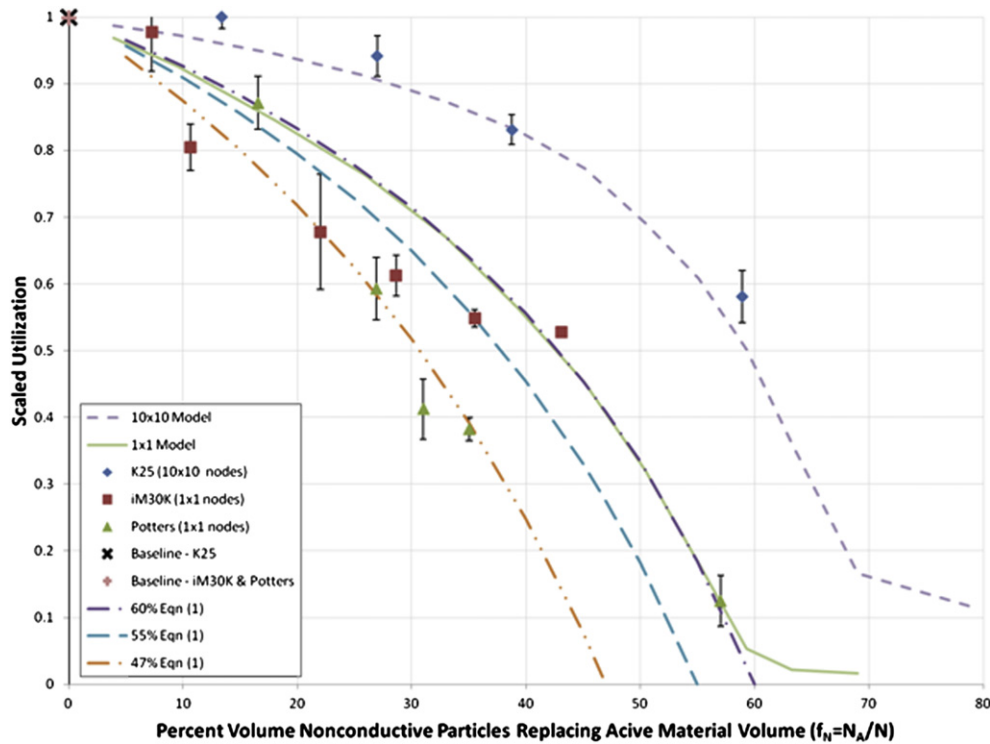


Fig. 14. Scaling of utilization compared to standard paste for various volume percentages and sizes of nonconductive additives.

HGMs with the maximum utilization we were able to obtain with hand pasted plates without additives (i.e. 54%).

When the hand pasted positive plates with the K25 HGMs (10×10 node size equivalent) were tested, the utilization of the plates decreased slowly with increasing amounts of additives as predicted by the model curve for large (10×10 node) additives. However, the experimental data is lower than predicted by the model. This should not be surprising as the model predicts 60% utilization when no additives are used whereas the measured data is 54% utilization for hand pasted plates without additives. While there is no comparable Eq. (1) for a 10×10 node size, the data for 10×10 node size additives can still be compared to the model predictions by scaling the experimental results of the K25 HGMs relative to the 54% maximum utilization achieved with non-additive plates fabricated during the same time period.

As mentioned previously in the discussion of Fig. 2, the fraction of the active material nodes replaced by the additives is dependent on the size of the additive. The horizontal axis of Fig. 13 is the number of active material nodes replaced by the additives divided by the total number of nodes, namely f_N . For all of the additives, the additive solid volume fraction, f_S , was used in this figure since it was simple to calculate and was known at the time of mixing. For small additives (approx. 1×1 node size), the value f_S closely approximates f_N , however; for large additives the value f_T is a better approximation. Unfortunately, measurements to estimate f_N were not performed at the time of the tests. We believe the results for the K25 HGM additives should therefore be shifted somewhat to the left since $f_T < f_S$, though by how much is unknown.

To account for variations in the paste that have nothing to do with the additive material, the utilization of paste containing the iM30K, Potters and K25 HGMs was scaled to the maximum utilization of non-additive paste plates fabricated at the same time as the additive plates, see Fig. 14. The utilizations of the iM30K and Potters HGM paste batches are compared to the utilization of the standard hand pasted plates made at the same time (47%).

Similarly, the utilization of paste having K25 HGM additives are compared to the utilization of later batch of standard hand pasted plates (54%).

Fig. 14 shows the results when this scaling is done so that all the utilizations are divided by the maximum utilization value. The scaled utilization value of one on the Y-axis of this chart represents the maximum utilization possible for that paste. Both the data and model are scaled by dividing the actual and predicted utilization by the critical volume fraction of that paste. In Fig. 14, this scaling is also shown for the critical volume fractions of 47%, 55% and 60%. The same standard deviation values from Fig. 13 are presented in Fig. 14. On several of the data points, the standard deviation is too small to see compared to the data point.

The Potters data between 10% and 40% is much lower than predicted by the model which assumes a 60% critical volume fraction but is consistent with the 47% $U_{\max}$ predictions from Eq. (1). The conglomeration of some of these particles as shown in Fig. 8 may have reduced the utilization in some plates. Referring back to Fig. 6, the model does predict slightly lower utilizations for 1×2 and 1×4 aspect ratio nonconductive additives, and the conglomerated Potters HGMs which form non-spherical masses at aspect ratios higher than one but on average less than ten may be causing a similar effect as a nonconductive fiber with an aspect ratio slightly higher than one.

Scaling the plate data to the hand pasted non-additive baseline plates provides a method by which all the data can be plotted on the same figure for different values of the maximum utilization. Notably, the test results for the K25 HGMs with an average size of 50–70 μm nonconductive additives show a good approximation to the scaled model results for “ 10×10 ” node size with an aspect ratio of one, see Fig. 14. The Potter's and filtered iM30K HGMs with an average size of 7 μm and 12 μm , respectively, represent the 1 node size and compare favorably with the Eq. (1) curve associated with the 47% maximum utilization paste. Although the model has a number of simplifying assumptions, the results of the plate

testing for the iM30K and Potters HGMs are qualitatively and surprisingly also quantitatively close to model predictions as shown in Fig. 14.

8. Summary and conclusions

Additives can be used in the electrodes of lead acid batteries to improve their porosity and/or increase their conductivity. Unfortunately for nonconductive porosity additives, an attendant drop in the critical volume fraction (CVF) is predicted from conductivity models. The increase in electrode performance at higher rates due to increased porosity may be partially offset by the drop in capacity due to a lower critical volume fraction. This paper provides information, both theoretical and experimental, that would allow an electrode designer to assess the drop in CVF and capacity when nonconductive additives including porous additives are used.

Nonconductive glass and hollow glass microspheres (HGMs) were added to the active material in the positive plates of lead acid batteries to investigate the effect they would have on the critical volume fraction. The solid volume percentage of various sizes of nonconductive additives was varied from 5% to 60% of battery paste volume. The utilization percentages of several plates were measured for each of the different volume percentages of the HGM nonconductive additives. The utilization of active materials, which is defined as the ratio of the discharge ampere-hours over the stoichiometric capacity of the active materials, was plotted with respect to different volume percentage and sizes of additives. The experimental data was compared with the theoretical values predicted by the two-dimensional conductivity model developed in previous work.

The change of utilizations with different volume percentage of additives provided qualitative results and near-quantitative results similar to those predicted by the model. An equation was given that provides a qualitative and near-quantitative predictor of utilization for 1×1 node size additives (i.e. approximately 5 μm diameter). When the results are scaled to account for variances in maximum utilization in paste having no additives made at the same time as the paste containing the additives, the results are quantitatively close to those predicted by the model. Therefore, the conductivity

model provides qualitative and near-quantitative prediction for the maximum utilization of paste containing nonconductive additives at various volume percentages.

Acknowledgements

We gratefully acknowledge the Office of Naval Research for their financial support of this work under the award “Advanced Lead Acid Battery Development for Military Vehicles” No. N00014-04-1-0612.

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